Application of Secondary Ion Mass Spectrometry in Studies of Niobium Segregation in Niobium-Doped Titanium Dioxide

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ABSTRACT
Secondary ion mass spectrometry (SIMS) is a powerful technique in the study of materials that demonstrate compositional changes as a function of depth from the surface. This is due to the high chemical sensitivity of SIMS (sensitive to ppb) and potential for high depth resolution. However, as a semi-quantitative technique, the application of SIMS to quantitative studies can be problematic without knowledge of the appropriate calibration information, which must be obtained through the use of carefully prepared reference specimens. In the present work, SIMS is used in the investigation of surface segregation in niobium doped polycrystalline TiO_2. This material has demonstrated important photo-catalytic properties with implications for alternative energy generation and environmentally-friendly water purification, but requires investigation in relation to surface versus bulk processing. The present paper demonstrates the use of SIMS in the quantitatively assessment of segregation in TiO_2 and the development of a calibration curve.

KEYWORDS: Titanium dioxide, niobium, segregation, calibration, photo-catalysis

INTRODUCTION

Awareness is growing that the functional properties exhibited by a material are often determined by the specific interface properties that prevail. For example, in a polycrystalline ceramic, the presence of secondary phases at grain boundaries can entirely determine the charge transport properties, regardless of the nature of the bulk phase. Similarly, the presence of surface phases can determine the way in which a material will interact with the ambient gas phase, irrespective of the properties of the bulk. Despite this seemingly obvious condition, investigations predominantly focus either on the processing and modification of bulk properties, in ignorance of the effect on surface properties, and vice versa. Hence, it is important to recognize the need to develop an understanding of the relationships that exist between bulk and surface processing.

Since the pioneering investigation of Fujishima and Honda [1] in 1972, which demonstrated that TiO_2 could be used to photo-electrochemically split water using ultra violet light, TiO_2 has been the subject of intense study [2, 3, 4, 5]. More recently, focus has shifted to the ability of TiO_2 to remove organics and bacteria from water [6] and to demonstrate self-cleaning [7] and superhydrophilitic [7] functions under sunlight. Whilst the potential applications of TiO_2 may be many and varied, one common element is the need to prepare TiO_2 that exhibits suitable surface properties in order to achieve the desired level of performance.

Secondary ion mass spectrometry (SIMS) is a highly sensitive surface analysis technique that enables the assessment of compositional changes in a material as a function of depth from the surface. In the present paper, the use of SIMS is considered for the investigation of niobium surface segregation in niobium-doped TiO_2. In particular, the issue of calibration is addressed, as this is critical if SIMS is to be used for quantitative assessment.

WHAT IS SECONDARY ION MASS SPECTROMETRY (SIMS)?

Secondary ion mass spectrometry (SIMS) is a powerful technique for characterising the surface and near surface region of solid materials. The significant advantage of SIMS is the combination of high elemental sensitivity (ppm and ppb) with high depth resolution (2-5nm). SIMS is also able to detect all elements from hydrogen to uranium.

Operating in ultra high vacuum, SIMS uses a continuous focused ion beam of Cesium or Oxygen to bombard the surface of the sample causing secondary ions to be ejected or 'sputtered' as the beam sputters progressively deeper into the sample. Simultaneous and continuous detection of these sputtered secondary

ions using a mass spectrometer provides an elemental depth profile of the sample from the surface into the bulk as a function of time.

SIMS has been used for many years in the microelectronics, optoelectronics and photovoltaics industry to characterise complex multilayered structures, surfaces and thin films. However, increasingly the advantages of the SIMS technique is being utilised as an important surface characterisation tool in a wide range of other areas of scientific research such as interfacial phenomena. Fig 1 illustrates the typical technical layout for a SIMS instrument.

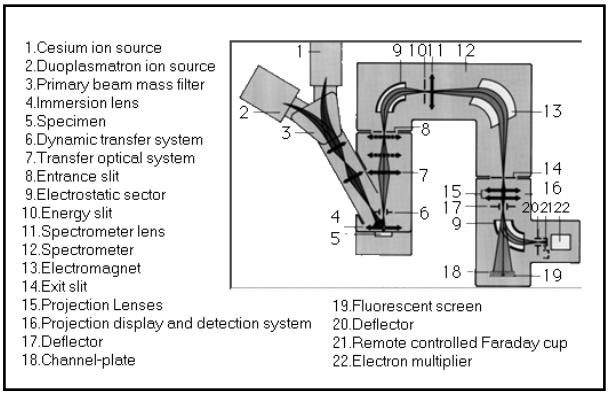

Fig. 1: Schematic technical layout for a typical SIMS instrument

REVIEW OF LITERATURE

Segregation is a mass transport phenomena in which point defects, such as dopant cations, are accumulated as interfaces during processing at elevated temperatures [8]. The minimization of interfacial free energy is the driving force for segregation, which is considered as a process of adsorption from the solid, rather than from the gas phase, which is more commonly considered. This is represented schematically in Fig 2.

The segregation of various impurity cations in TiO_2 has been investigated by a number of research groups [9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. A comprehensive review of this literature has already been reported [8]. Whilst the quantity of available information on segregation in TiO_2 is reasonable, it is difficult to reliably interpret this information due to the common failure to assess equilibrium segregation. In all reported cases, the segregation behaviour observed is a snapshot of a dynamic process occurring under specific processing conditions of temperature, oxygen activity (p(O2)) and time (which are not always adequately disclosed). Consequently, the observed behaviour represents transient phenomena which are difficult to widely reproduce and understand. However, equilibrium segregation, which represents a steady state condition defined by temperature and oxygen activity ($p(O_2)$) is more easily reproduced as this behaviour is independent of previous processing.

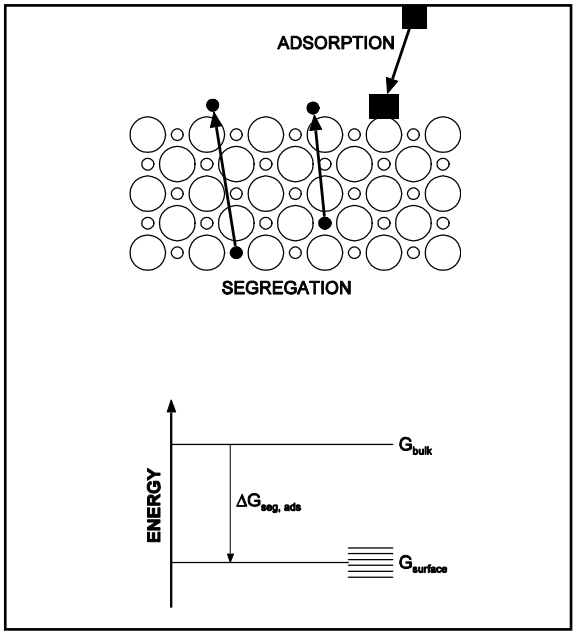

Fig. 2: Schematic illustration of segregation and adsorption and the associated change in interfacial free energy

In addition to the processing conditions of temperature and $p(O_2)$, microstructure can play an important role. As demonstrated by Terwilliger and Chiang [19,], the size of grains can significantly influence the behaviour of segregation. These investigators observed for Ca segregation, that a grain size of 150 – 350 nm is critical, with the exsolution of CaTiO3 occurring when this critical grain size is exceeded. This phenomenon is clearly related to the ability of grain boundaries to dissolve Ca, but it is complicated by the kinetics of grain boundary migration and the competing kinetics of segregation. Irrespective, this work demonstrates the need to relate microstructure to segregation during surface versus bulk processing.

Frequently, the reported literature on segregation in TiO2 involves the use of techniques such as x-ray photoelectron spectroscopy (XPS) [**Error! Bookmark not defined.**,**Error! Bookmark not defined.**,**Error! Bookmark not defined.**,**Error! Bookmark not defined.**]. While this technique is highly sensitive to changes in material composition, its depth profiling capabilities are limited beyond depths of ~ 5-10 nm. For segregation, this level of performance may be adequate depending on the case at hand, but could be

expected to be too shallow. The use of SIMS for segregation studies has not been so widely applied for TiO2, with only Bernasik et al [**Error! Bookmark not defined.**] reporting in the literature. However, with its high suitability for depth profiling, SIMS appears to be a highly appropriate technique for segregation studies where the depth of segregation is unknown.

EXPERIMENTAL PROCEDURE

Preparation of Specimens

Nb-doped TiO_2 powders were prepared by the sol-gel method from the hydrolysis of Ti-isopropoxide (97% - Aldrich) mixed with sufficient $NbCl_5$ (99% - Aldrich) to precipitate doped TiO_2 powders. Mixtures of ti-isopropoxide, ethanol and $NbCl_5$ were combined and stirred at room temperature, before being gently heated to 373 K, until the mixture became no longer fluid. The temperature was then increased to 383 K and the mixture was left to fully dry, producing the doped powder. The powders were then calcined at 900°C for 2.5 hours under an oxygen atmosphere, after which they were uniaxially dry pressed to approximately 40 MPa, before cold isotatic pressing to 400MPa. The pellets were then sintered at 1773 K in air for 5 hours. After sintering, the specimens were polished to a high mirror finish. Surface analysis was initially performed on the as-polished surfaces to establish the bulk yields. Afterwards, the specimens were re-polished, annealed at 1273 K for 20h in different conditions of oxygen activity and analysed again to establish the effect of processing on the surface concentration profile.

Chemical Analysis

To accurately establish the bulk Nb content in the specimens, ion-coupled plasma mass spectrometry (ICP/MS - Perkin Elmer Elan 6000) was used. This was performed on a small sample of each of the calcined powders, which were firstly dissolved in a 1:1 mixture of lithium metaborate and lithium tetraborate powders in a platinum crucible at 1373 K for 1 hour. Once cool, the fused samples were removed from the crucible and dissolved in a solution of concentrated HNO_3, HF and distilled water. The solutions were then analyzed using ICP/MS.

Surface Analysis

Surface analysis was performed using SIMS (Cameca IMS-5f). The primary ion beam consisted of Cs^+ ions with a net impact energy of 3keV and a raster area of 250μm x 250μm. Typical ion beam currents ranged from 10 nA to 32 nA. In order to reduce the possibility of 'edge effects', aperture and lens settings were applied to only admit positive secondary ions into the mass spectrometer from a circular area of 55μm diameter within the rastered region. The instrument was operated at a working pressure of 10^{-9} Torr with a mass resolution of M/ΔM ~300 and energy bandpass of 130eV. To minimise surface charging, the specimens were coated with gold (5-10nm thick). After sputtering, the crater depth was determined from the average of several surface profiles obtained using a profilometer (Dektak Alpha Step). The gold coating was not removed prior to profilometry since it helped to identify the SIMS craters. The gold coating was removed prior to each annealing treatment using warm (~323 K) *aqua regia.*

RESULTS AND DISCUSSION

Fig 3 illustrates a typical output from SIMS analysis indicating traces for Nb, Ti and O atoms within a TiO_2 lattice in terms of intensity (counts per second) as a function of analysis time (seconds). In order to make quantitative assessment of this data, the "intensity" axis must be calibrated for species concentration, while the "time" axis must be calibrated for depth.

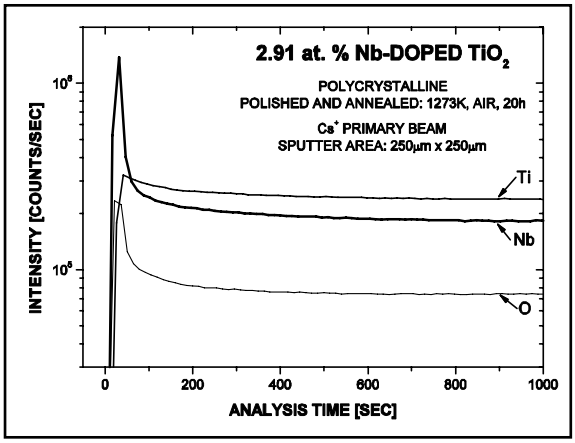

Fig. 3: Typical SIMS output after analysis

Concentration Calibration

In order to calibrate the intensity data obtained using SIMS to the actual concentrations of species of interest, a calibration curve must be generated. This curve graphically relates the actual concentration of a particular species to the intensity signal it would generate during analysis with SIMS. This can only be achieved using well defined reference specimens which must be prepared in such a manner that they are reliable representations of the system to be studied. Hence, the concentration of the element of interest must be accurately known, ideally determined with high accuracy through the use of a sensitive chemical analysis technique such as ion-coupled plasma mass spectrometry (ICP-MS) following any high temperature processing. The matrix chosen for reference specimens should also be the same as the studied system in order to eliminate matrix effects

associated with preferential sputtering of particular lattice elements during SIMS analysis.
For studies of segregation, as in the present case, reference specimens can be prepared and subsequently used as part of the primary investigation. This has two main advantages:

- Matrix consistency. As both the reference specimens and the studied specimens are the same, matrix effects are completely eliminated.
- Bulk compositional consistency. The bulk composition of the reference material and studied specimen is identical, which dramatically reduces any uncertainties associated with the chemical analysis and the SIMS analysis.

Fig 4 illustrates the intensity of Nb (normalized against the matrix cation, Ti) obtained using SIMS for the various reference specimens prepared in the present project. Aside from some initial intensity perturbation associated with surface damage caused through polishing, the traces for each specimen assume steady intensity values that are related to the bulk composition of the specimens. By taking each of these steady state intensity values, and plotting them against the corresponding Nb concentration, the calibration curve is generated. This is illustrated in Fig 5. As seen, a close linear fit is obtained between the actual Nb concentration and the intensity obtained by SIMS. This fit may then be used to relate the measured intensity obtained during depth profiling to the unknown Nb concentration profile encountered in these specimens as a result of segregation.

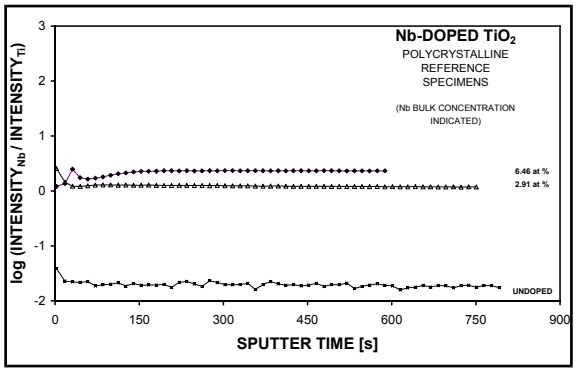

Fig. 4: SIMS analysis of Nb-doped TiO_2 reference specimens

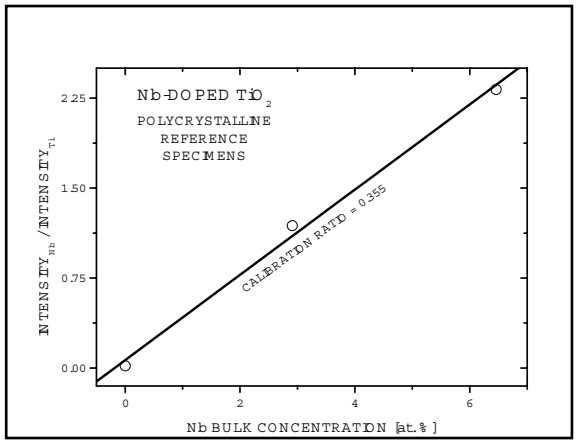

Fig. 5: Calibration curve obtained for Nb-doped TiO_2 reference specimens

Depth Calibration

As seen in Figure 3, a typical SIMS depth profile is related to sputtering time. In order to quantify this to actual depth from the surface, a depth calibration must be performed. This requires the determination of the sputtering rate. During SIMS analysis, a sputter crater is formed due to the bombardment of primary ions. By determining the depth of the sputter crater, a sputtering rate can be simply calculated. However, this rate is an average value which may or may not be accurate during the profile. The ideal case would be to determine sputtered depth "in situ" during analysis, however this is presently beyond the capability of the SIMS technique. Alternatively, the determined sputtering rate could be improved by determining an average sputtering rate over shorter analysis depths by intermittently halting analysis, and measuring the crater depth. This approach lacks practical feasibility due to difficulties in the re-establishment of identical sputtering conditions upon resumption of analysis. Furthermore, it may be difficult to accurately assess the small changes in crater depth.
Fig 6 displays the shape of a sputter crater determined using profilometry. As seen, the shape of the crater is strongly influenced by the surface roughness, which impacts on the accuracy to which the crater depth may be assessed. For comparison, a sputter crater with low surface roughness is illustrated in Fig 7 [20]. Hence, for reliable depth calibration, high surface finish is desirable. This is also the case for SIMS and many other surface sensitive techniques in general.

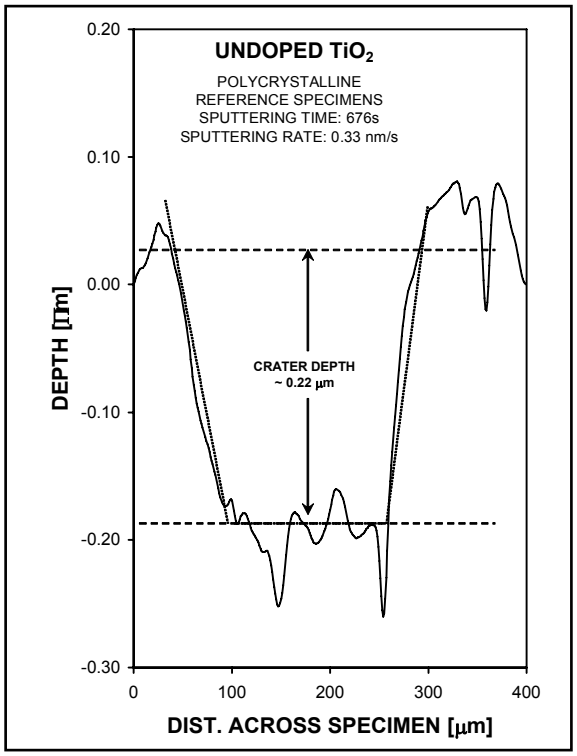

Fig. 6: Sputter crater obtained for Nb-doped TiO_2 reference specimens

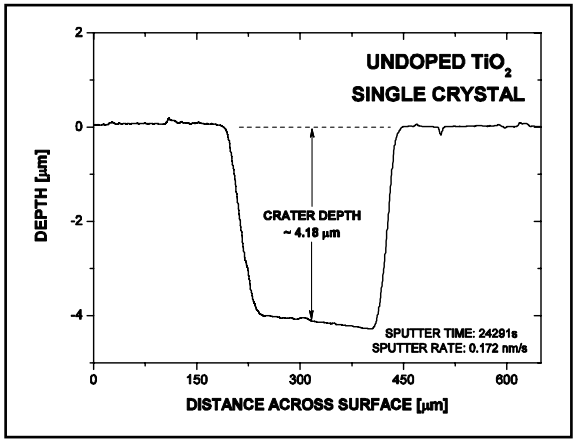

Fig. 7: Sputter crater obtained by Sheppard et al [20]

Quantification

Once both the concentration calibration and the depth calibration have been performed, then SIMS data may be used for quantitative analysis. Considering the case of Nb surface segregation in TiO_2, Fig 8 illustrates a quantitative depth profile based on obtained SIMS data. As seen, the approach to SIMS calibration is highly useful for the assessment of segregation, which is clearly displayed in this figure.

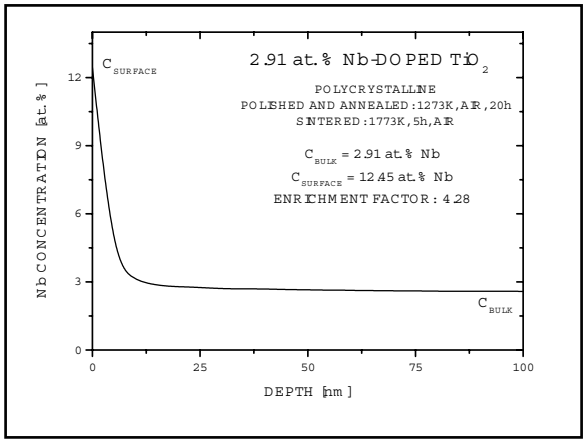

Fig. 8: Nb surface segregation in 2.91 at. % Nb-doped TiO_2

CONCLUSIONS

The present paper has considered the use of secondary ion mass spectrometry (SIMS) for the study of segregation. As an example, Nb surface segregation in TiO2 has been investigated. It has been shown that in order to use SIMS for quantitative investigations, both a concentration calibration and a depth calibration must be performed. Each calibration must be considered closely in order to minimize sources of uncertainty and improve the reliability of the calibration. However, practicalities can pose limiting factors, especially when performing the depth calibration.

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